

ARYL HALIDES |

Structure

14.1	Introduction	Electrophilic Substitution Reactions
	Expected Learning Outcomes	Reactions due to C-X bond
14.2	Structure and Reactivity	
14.3	Preparation of Aryl Halides	14.5 Reactivity and Relative Strength of C-X Bonds in Halogen Derivatives
14.4	Reaction of Aryl Halides	
	Nucleophilic Substitution by Addition-Elimination	14.6 Summary
	Nucleophilic Substitution <i>via</i> Benzene Intermediate	14.7 Terminal Questions
		14.8 Answers

14.1 INTRODUCTION

In Unit 13, we have pointed out that there is a difference in the nature of C-X bond of aryl halides and alkyl halides. Because of this aryl halides differ from the alkyl halides in their preparation and properties. In this Unit, we will study the unique chemistry of aryl halides.

First, we shall take up the structure and reactivity of aryl halides, which is followed by their preparations and properties. At the end of the unit we shall compare the reactivity and relative strength of C-X bond in different type of halogen derivatives.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ explain why aryl halides are less reactive than alkyl halides,
- ❖ outline the methods of preparation of aryl halides,
- ❖ describe the reactions of aryl halides, and
- ❖ explain the difference in structure and reactivity of alkyl, alkenyl and aryl halides towards nucleophilic substitution reactions.

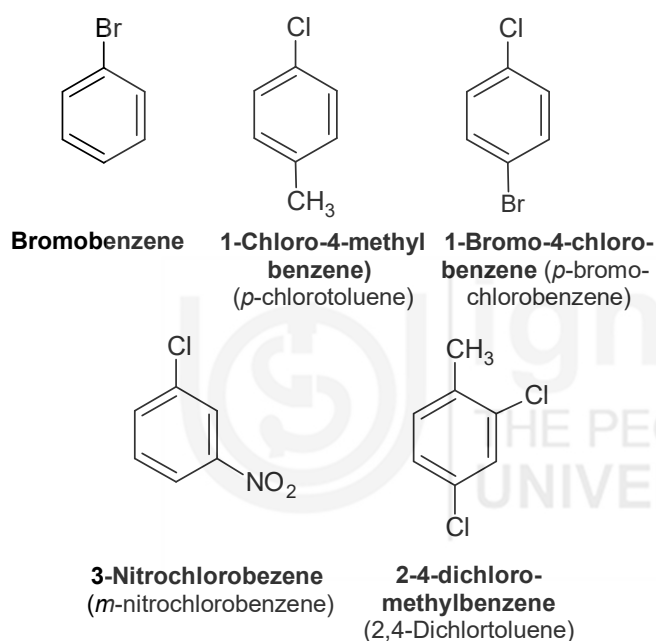
14.2 STRUCTURE AND REACTIVITY

Before going into the details of the preparations and properties of aryl halides let us take a look at the structure and reactivity of these compounds so that we can understand why their reactions are different from alkyl halides.

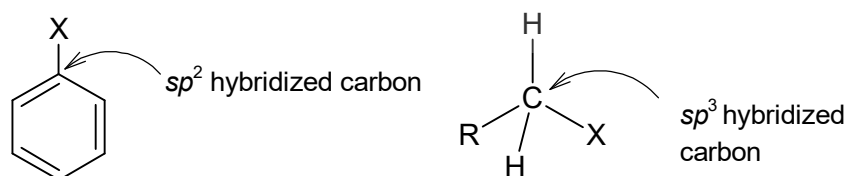
Compounds in which one or more hydrogen atoms of an aromatic ring are replaced by halogen atom(s) are called aryl halides. These compounds are also known as **haloarenes** and have the general formula, Ar-X .

Just to recall, in IUPAC naming of halogens, the prefix – chloro, bromo, iodo etc. is added before the name of arene. The relative position of halogen atoms are indicated by numbers. The prefixes *ortho* (*o*), *meta* (*m*) and *para* (*p*) are also used to indicate the relative positions of substituents.

Some representative examples are given below:

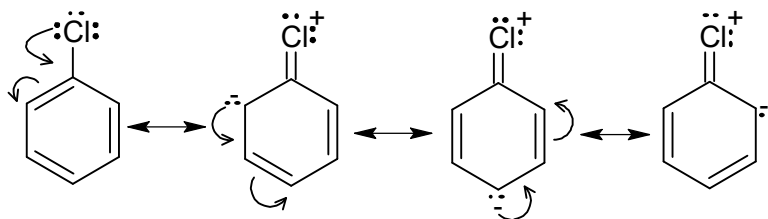


Now, let us focus our attention on the structure and reactivity of aryl halides. It has been discussed earlier that C–X bond in the aryl halide is shorter and stronger because of the difference in hybridisation of carbon atom in C–X bond. In alkyl halides, the carbon atom attached to halogen is sp^3 hybridised while in case of aryl halides, the carbon atom attached to halogen is sp^2 -hybridised.

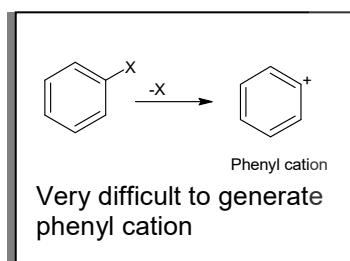


The sp^2 hybridised carbon with a greater *s*-character is more electronegative and can hold the electron pair of C–X bond more tightly than sp^3 -hybridised carbon in alkyl halide with less *s*-character. Besides this factor, the unbounded *p*-orbital having electron pairs of the halogen atom can overlap with the π system of the aromatic ring. This will provide partial double bond character in C–X bond (C–Cl bond length in alkyl halide is 177 pm while in aryl halide is 169 pm). The partial

double bond character of C-X bond can be explained by drawing resonating structures for chlorobenzene. The electron pairs on chlorine atom are in conjugation with π -electrons of the ring and the following resonating structures are possible:



Because of these two factors, the C-X bond in aryl halides becomes shorter and stronger in comparison to C-X bond of alkyl halides. Since it is difficult to break a shorter and stronger bond, therefore, aryl halides undergo relatively few reactions involving the carbon-halogen bond.



Aryl halides do not undergo substitution by either the S_N1 or S_N2 pathways that are characteristic of nucleophilic substitution reactions in alkyl halides.

Elimination reactions also do not occur in aryl halides. Under certain conditions, they do undergo nucleophilic substitution reactions by different mechanism. The reason for the lack of S_N1 reactivity of aryl halide is the difficulty in generation of phenyl cation from a corresponding aryl halide. Phenyl cation, if so formed, as a result of self-ionisation will not be stabilised by resonance. Further, the electron rich aromatic ring reduces δ^+ on carbon atom of C-X bond and also repel approaching electron rich nucleophile for its back side attack (condition needed for S_N2 reaction).

The aromatic ring of aryl halides will react same way as in benzene and will undergo electrophilic substitution reactions. In these reactions, halogens influence the reactivity and orientation. The halogens are relatively electronegative and have an electron withdrawing inductive effect. Therefore, they deactivate aromatic ring system. On the other hand through its resonance effect halogens activate aromatic ring system. Thus, the inductive and resonance effects of the halogen are counter to each other, but the former is stronger than the latter. Thus the halogens weakly deactivate the ring, and are *ortho-para* directing during electrophilic substitution reactions.

SAQ 1

How do you account for the fact that aryl halides are less reactive towards nucleophilic substitution reactions under ordinary conditions?

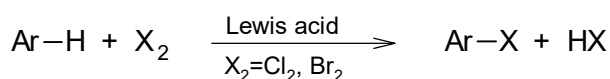
SAQ 2

Give explanations for the lack S_N1 and S_N2 reactivity of aryl halides.

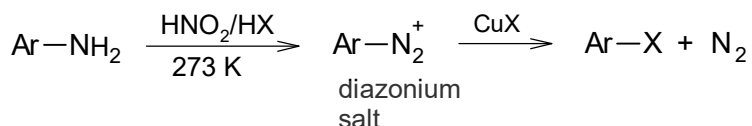
14.3 PREPARATION OF ARYL HALIDES

Aryl halide may be prepared by one of the methods given below in Table 14.1

Table 14.1: Preparation of Aryl halide

From Aromatic Hydrocarbons (Direct Halogenations Method)

Lewis acid = FeCl_3 , AlCl_3 , $\text{Ti}(\text{OAc})_3$ etc.

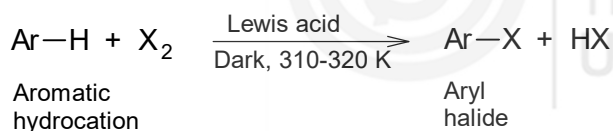
From Aromatic Amines (Diazonium salt method)

CuCl , CuBr

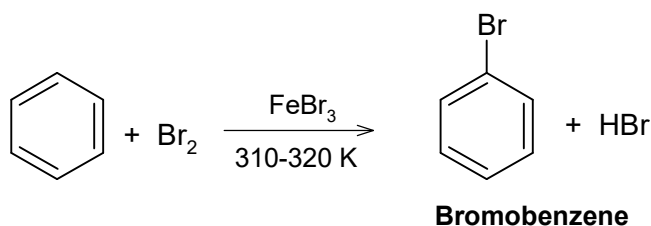
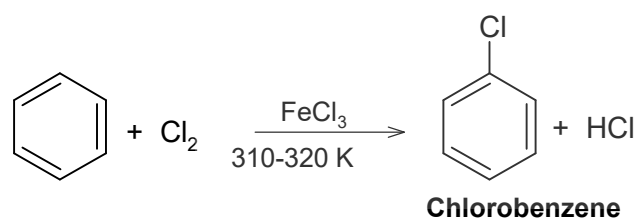
The main drawback of direct halogenations is to get single halogenated product. Generally, with mono-halogenated products, mixture of *ortho* and *para* dihalogenated products are also formed. Thus diazonium salt method is preferred for the preparation of aryl halides.

Let us briefly consider these methods of preparation.

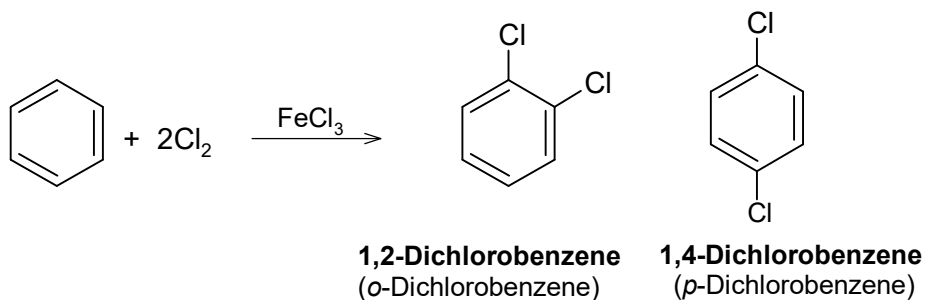
- i) **From Aromatic Hydrocarbons:** As discussed in Unit 11, the aromatic halogenation of aromatic hydrocarbon needs the assistance of a Lewis acid as a catalyst. Generally ferric halides or aluminum halides are used as catalysts (FeCl_3 , FeBr_3 , AlCl_3 etc.).



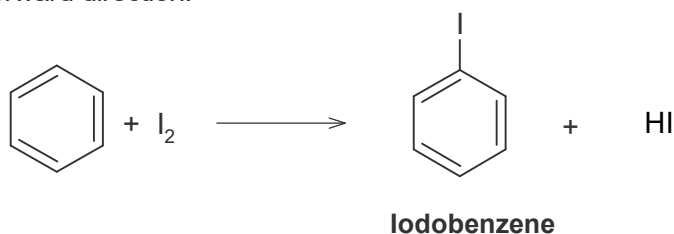
In actual practice, iron filings in the presence of chlorine or bromine are commonly used. The halogens react with iron filing to form corresponding Lewis acid.



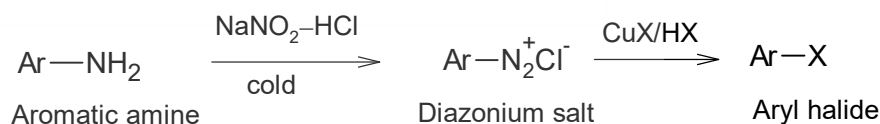
If two moles of chlorine (per mole of benzene) are used, a mixture of *ortho*- and *para*-dichlorobenzene is obtained in which the *para* compound predominates for steric as well as electronic reasons.



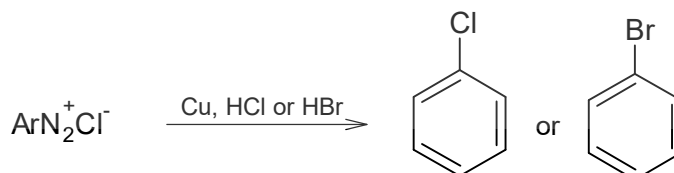
Fluorobenzene and iodobenzene are difficult to prepare by direct fluorination and iodination. The reaction with fluorine is violent and cannot be controlled. Reaction of iodination is reversible. This reaction is carried out in the presence of oxidizing agents such as iodic acid or nitric acid which oxidises HI formed in the reaction to iodine enabling the reaction to proceed in the forward direction.



- ii) **From Aromatic Amines:** In this process the amine is first converted to the diazonium salt (ArN_2^+X^-), which is then converted to aryl halide using the solution of cuprous halide dissolved in the concentrated halogen acid. This method is known as **Sandmeyer reaction**.



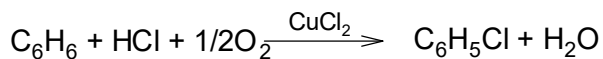
Copper powder can also be used in place of cuprous halide. This modified reaction is called **Gattermann reaction**.



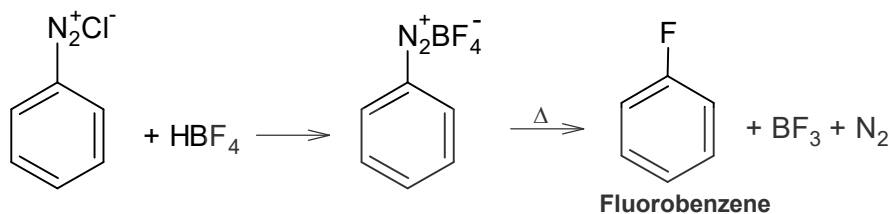
Replacement of the diazonium group by $-\text{I}$ does not require the use of a cuprous halide.



Chlorobenzene is prepared commercially by the **Rasching process** in which a mixture of benzene vapour, air and hydrogen chloride is passed over copper chloride.



Fluorobenzene cannot be prepared by either Sandmeyer reaction or Gattermann reaction. For preparing fluorobenzene, benzene diazonium chloride is treated with fluoroboric acid. This reaction produces diazomium fluoroborate which, on heating, produce fluorobenzene. This reaction is called **Balz-Schiemann reaction**.



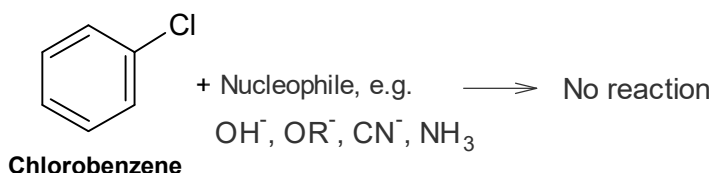
SAQ 3

How the following conversions can be carried out?

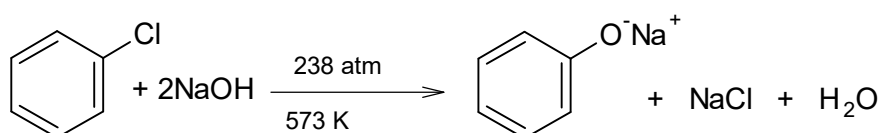
- Aniline to chlorobenzene
- Benzene to Iodobenzene
- Aniline to Fluorobenzene

14.4 REACTION OF ARYL HALIDES

As discussed earlier, the aryl halides are relatively unreactive towards nucleophilic substitution reactions; they do not react under ordinary conditions with NaOH, $\text{C}_2\text{H}_5\text{ONa}$, NaCN, NaSH, H_2O , or NH_3 .



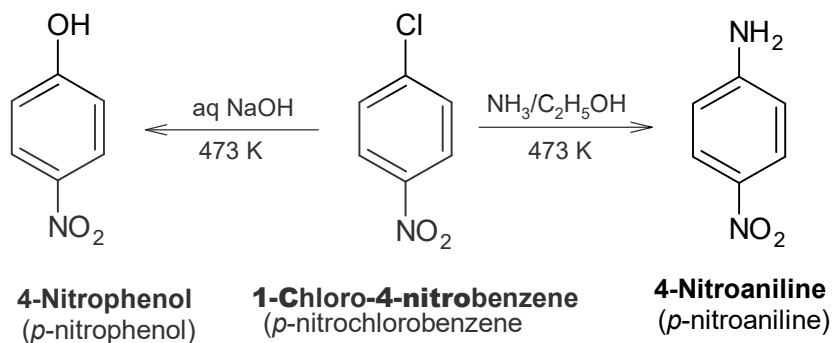
Aryl halides may be forced to react with nucleophiles under drastic conditions such as with very strong base (NaNH_2) or with moderate base (NaOH) at high temperature and pressure. For example, chlorobenzene when heated at 573 K under high pressure with NaOH, it is converted to sodium phenoxide. Neutralisation of this salt gives phenol.



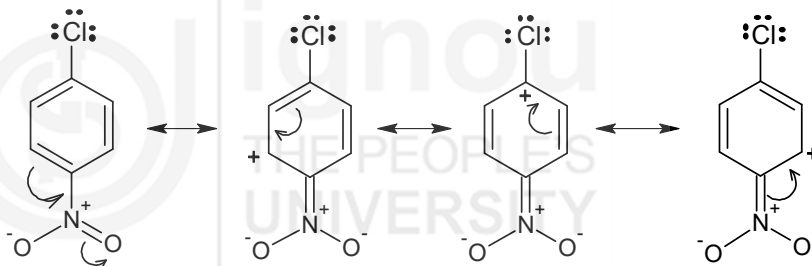
We have already mentioned the possible explanations of the low reactivity of aryl halides in earlier section. In above example, the chlorine atom in the C-Cl group is more tightly bound in Ar-Cl than in C-C-Cl because of the higher s character of sp^2 carbon of benzene ring. Another explanation was given that due to resonance,

the carbon-halogen bond in aryl halides acquires partial double-bond character and hence the halogen atom is more strongly bound to carbon as compared to alkyl halides in which no resonance of this type exists. We also mentioned that electronegative halogen atom deactivates the benzene ring.

On the other hand, when a strong electron withdrawing group is present at *ortho* and/or *para* to the halogen atom in an aryl halide, the replacement of halogen by nucleophilic reagents is facilitated, e.g.



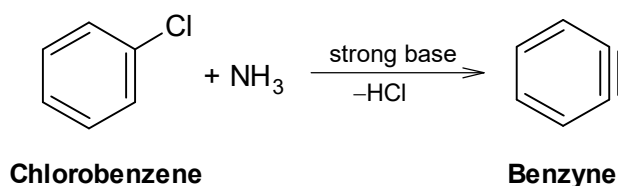
The resonance forms for the starting material (*p*-nitrochlorobenzene) indicate a low electron density at the halogen-bearing carbon. Similar forms can be written for the *o*-nitrochlorobenzene.



Resonance structure of 1-chloro-4-nitrobenzene (*p*-nitrochlorobenzene)

As shown above, the presence of nitro groups at *ortho*-position(s) and/or *para*-position withdraws the electron density from the benzene ring and thus creates intense positive charge on the carbon attached to chlorine. This facilitates the attack of the nucleophile on carbon attached to chlorine.

Nucleophilic aromatic substitutions do not follow S_N1 and S_N2 pathways. They occur by two different mechanisms: The **addition elimination mechanism** and the **benzyne intermediate mechanism**, which involves the highly reactive elimination reaction intermediate, **benzyne**.



The aromatic ring to which halogen is attached can undergo typical electrophilic aromatic substitution reactions, which we have already discussed in Units 11 and 12. As you would recall, the halogen is deactivating and *ortho*, *para* directing. Now,

we will take up reactions of aryl halides in some more detail.

SAQ 4

Explain why the dipole moment of chlorobenzene is lower than that of chlorocyclohexane?

SAQ 5

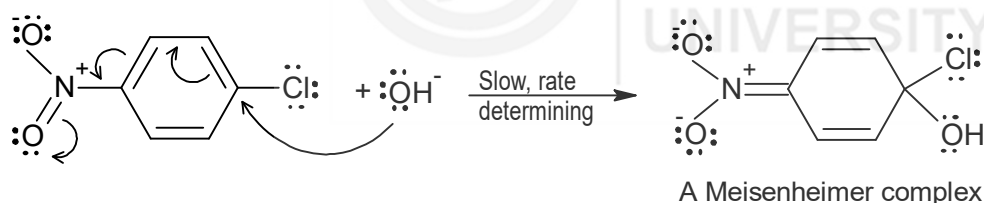
Write the resonating structures for 3-chloronitrobenzene. Compare these structures with 4-chloronitrobenzene and give reason why nitro group at 3 position is not effecting reactivity of 3-chloronitrobenzene for nucleophilic substitution reactions?

14.4.1 Nucleophilic Substitution by Addition – Elimination

Now consider again the example of 1-chloro-4-nitrobenzene. When this compound is treated with aqueous sodium hydroxide (15 %), it is converted into 4-nitrophenol (*p*-nitrophenol). Such reactions occur in two steps: nucleophilic addition is followed by elimination. Step one is the slow and therefore it is rate determining step.

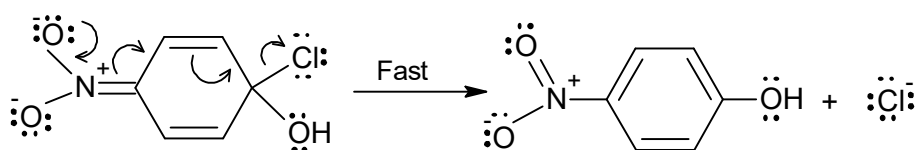
Mechanism: Nucleophilic Aromatic Substitution by Addition-Elimination

Step 1: Bond formation between hydroxide ion (a nucleophile) and carbon of C–X bond (an electrophile)



The intermediate complex is stabilized by a resonance interaction with nitro group. Such intermediates are named Meisenheimer complexes after the German Chemist who first characterised them. You can see how nitro group at *para* position is participating in delocalisation of the negative charge in the complex.

Step 2: Elimination of halide ion (leaving group) to regenerate aromatic ring and formation of phenol.

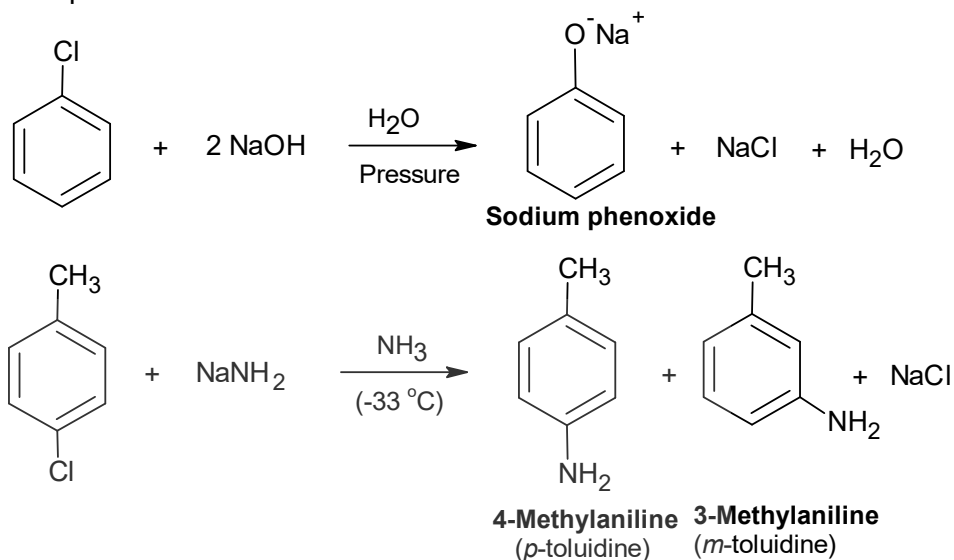


14.4.2 Nucleophilic Substitution *via* Benzyne Intermediate

Aryl halides not having any strong electron withdrawing group at *ortho*- and

para- positions undergo nucleophilic substitution reaction *via* benzene intermediate.

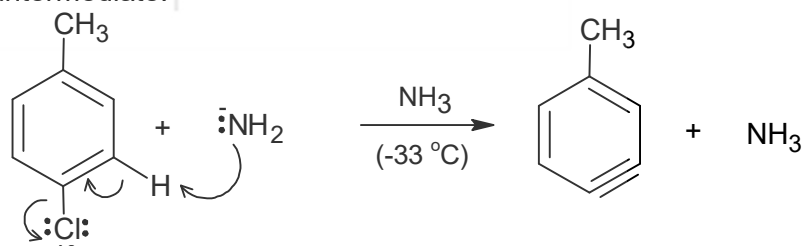
Examples:



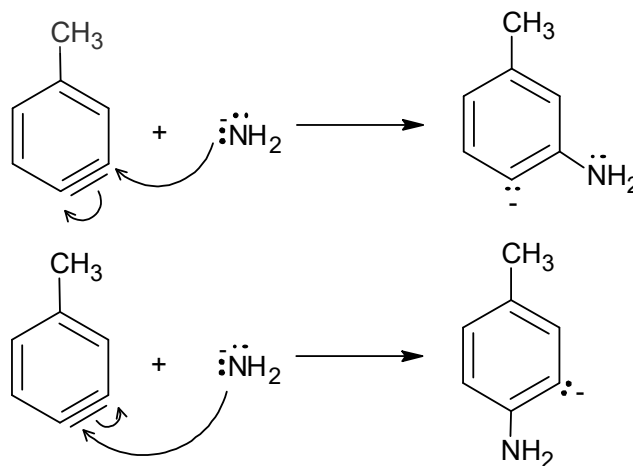
In second example you may have noticed that nucleophilic (NH_2^-) is not only attacking at the carbon centre of C—X bond but also at a position adjacent to it. To account for such experimental observation, it has been proposed that elimination of HX occurs to form a benzyne intermediate which then undergoes nucleophilic addition to the triple bond to give the products shown above.

Mechanism: Nucleophilic aromatic substitution *via* Benzyne Intermediate

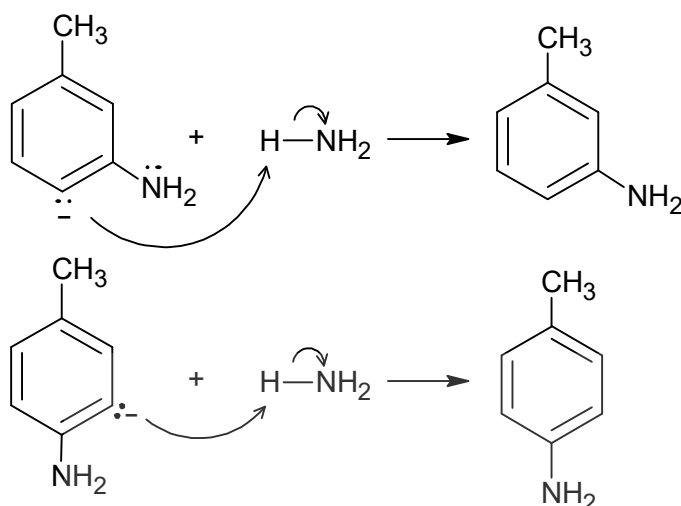
Step 1: Dehydrohalogenation of the benzene ring to form a benzyne intermediate.



Step 2: Amide ion (nucleophile) can attack both the carbon centres of triple bond to form two carbanion intermediates.

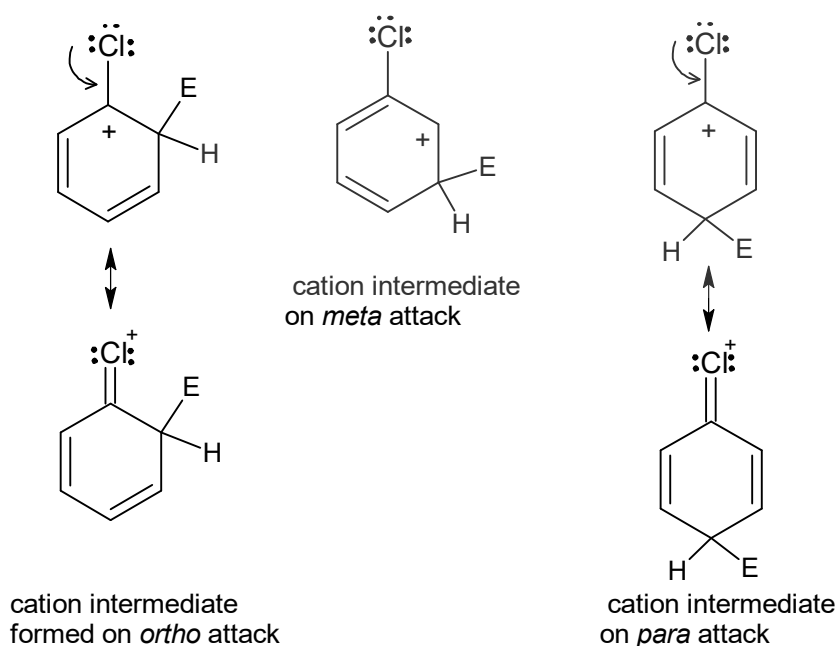


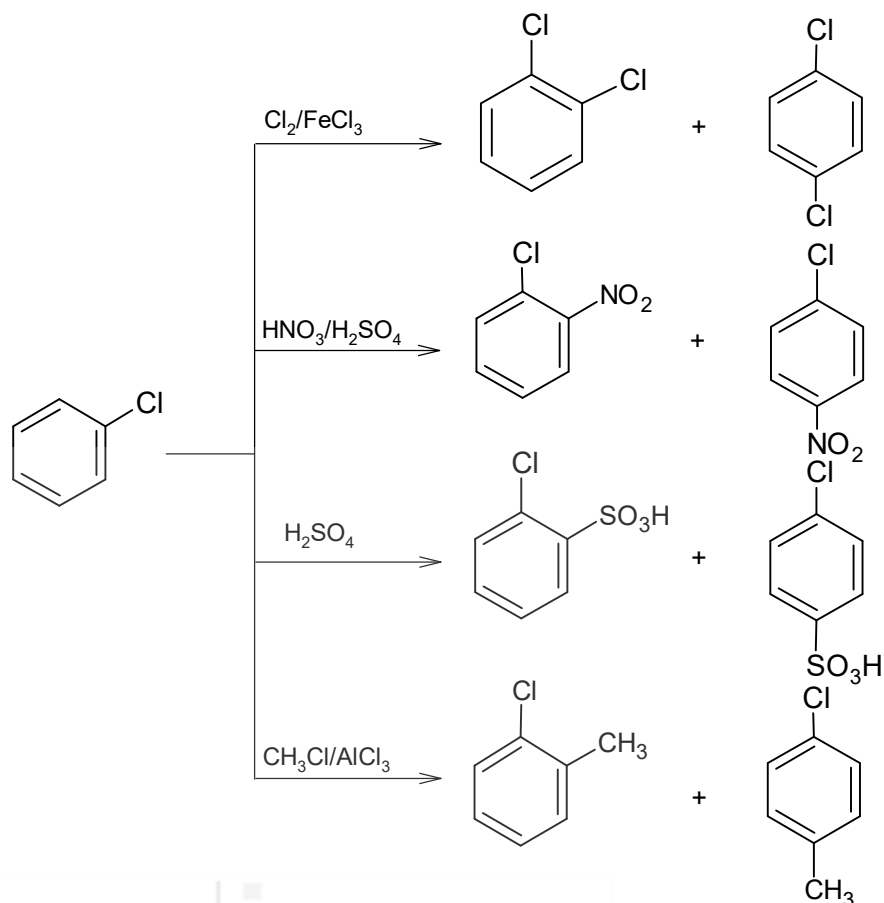
Step 3: Carbanions so formed abstract protons from ammonia to give final products.



14.4.3 Electrophilic Substitution Reactions

Similar to benzene, the benzene ring of chlorobenzene undergoes electrophilic aromatic substitution reaction. The most common electrophilic substitution reactions in chlorobenzene are halogenations, nitration, sulphonation and Friedel Crafts reaction. We have already discussed that chloro group in chlorobenzene is weakly deactivating and *ortho* and *para* directing. Because of this we need more drastic reaction conditions. *Ortho* and *para* directing orientation of chloro group for electrophilic aromatic substitution can be explained on the basis of the relative stability of carbocation intermediates formed by attack of electrophile on chlorobenzene. A chlorine *ortho* or *para* to the site of electrophilic attack can help to stabilise the carbocation intermediate by delocalization of the positive charge through resonance involving unshared electron pairs. Such stabilisation is not possible in carbocation intermediate formed on meta attack.



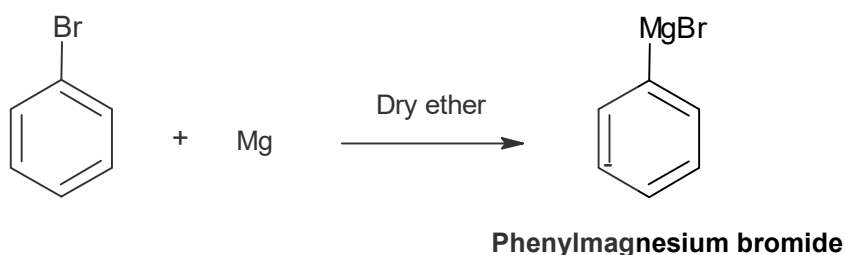


These reactions follow the mechanics discussed for the electrophilic addition reactions of benzene.

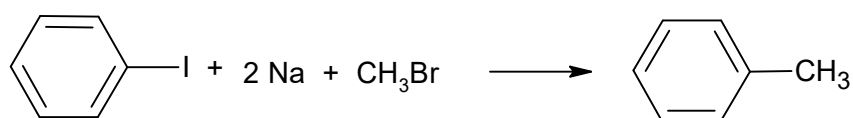
14.4.4 Reactions due to C-X Bond

Besides the substitution reactions, aryl halides undergo reaction with metals to form organometallic compounds.

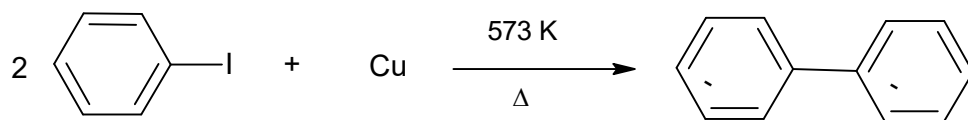
Bromo- and Iodobenzene: They react with magnesium metal to form Grignard reagents. Chlorobenzene is relatively unreactive.



Aryl halides react with alkyl halide in the presence of sodium metal to yield alkyl benzene. This reaction is known as Wutz- Fittig reaction. It is a modification of the Wurtz reaction which you have studied earlier.



Aryl halides on heating with copper powder give diaryls. This reaction is known as Ullmann reaction.



SAQ 6

How will you bring about the following conversions?

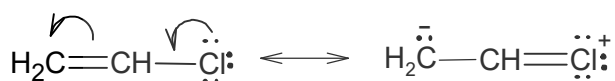
- Iodobenzene to biphenyl.
- Bromobenzene to phenylmagnesium bromide
- Benzene to 1-bromo-4-nitrobenzene

14.5 REACTIVITY AND RELATIVE STRENGTH OF C-X BONDS IN HALOGEN DERIVATIVES

Before taking up the reactivity and relative strength of C-X bond among halogen derivatives let us also understand the nature of alkenyl and alkynyl halides.

Alkenyl and alkynyl halides also similar to aryl halides and are less reactive towards nucleophilic substitution reactions and do not undergo $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ reactions.

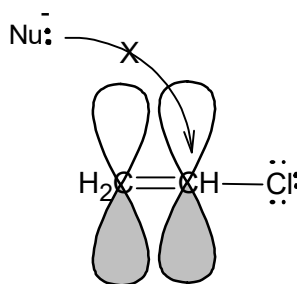
In general, similar to aryl halides, C-X bonds are shorter and stronger in alkenyl and alkynyl halides because i) in alkenyl halide, carbon attached to halogen is sp^2 hybridised and in alkynyl halide it is sp hybridised; ii) the C-Cl bond acquires partial double bond character due to resonance. As a result, the bond cleavage in alkenyl and alkynyl halide are difficult than alkyl halides and therefore, they are also less reactive towards nucleophilic substitution reaction. Both, alkenyl halides and alkynyl halides do not undergo $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ reactions.



Resonating structures of chloroethene

Lack of $\text{S}_{\text{N}}1$ and $\text{S}_{\text{N}}2$ reactivity of alkenyl halides and alkynyl halides can also be explained on the basis of the ease of formation of transition states.

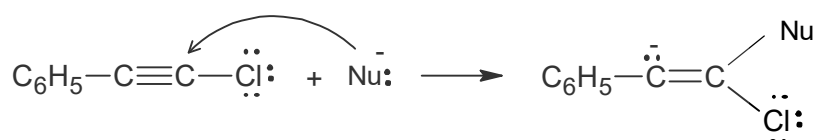
Because of the high s character of double and triple bonded carbons, they are stronger electron – attracting centres than saturated (sp^3) carbon, that is the reason alkyne and alkenes are stronger acids than alkanes. Therefore, it will be much more difficult to generate carbocations such as $\text{CH}_2 = \text{CH}^+$ and $\text{HC} \equiv \text{C}^+$ from the corresponding halides. Thus, this factor supports the lack of $\text{S}_{\text{N}}1$ reactivity of alkenyl and alkynyl halides. Further, p orbitals of carbon double and triple bond block the back side attack of nucleophile as shown below. This factor explains the lack of $\text{S}_{\text{N}}2$ reactivity in alkenyl and alkynyl halides.



Under drastic conditions, substitution of the halogens occurs in alkenyl and alkynyl halides. Such reactions follow different mechanism. In these cases, the nucleophile first adds to the carbon centre of C–X bond, and in a subsequent step the halogen leaves as halide ions. This is an “addition – elimination” mechanism.

Step 1:

Addition



Step 2:

Elimination



From our discussion on the nature and reactivity of alkyl, aryl, alkenyl and alkynyl halides, it can be concluded that the relative reactivity of halogen derivatives can be predicted on the basis of the following factors:

- (i) s character of hybridised carbon attached to halogen
- (ii) Resonance effect
- (iii) Stability of carbocation formed on self ionisation of C–X bond (condition for S_N1 reaction)
- (iv) Feasibility of back side attack on C–X bond (condition for S_N2 reaction)

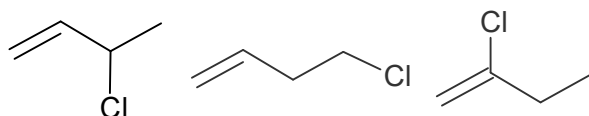
The C–X bond of alkenyl, alkynyl and aryl halide is shorter compared to alkyl halides because the carbon attached to halogen is either sp^2 or sp hybridised. Resonance effect also contributes in increasing bond strength of C–X in these compounds. Lack of stability of carbocation, if formed, on self ionisation and lack of feasibility of backside attack of nucleophile on C–X bond explain that these compounds are less likely to follow S_N1 and S_N2 mechanisms.

In the Table 14.1 below, we have listed bond length and bond strength of each class of halogen derivatives.

Compound	C-X bond length (pm)	Bond Strength/kJ mol ⁻¹
C ₂ H ₅ - Cl	177	340
CH ₂ = CH- Cl	169	435
HC≡ C- Cl	163	--
C ₆ H ₅ - Cl	169	465

SAQ 7

Arrange following halides in order of expected increasing reactivity towards sodium iodide.



14.6 SUMMARY

In this unit, we have described the chemistry of aryl halides. We are summarizing below what we have studied:

- Aryl halides can be prepared from aromatic hydrocarbons by direct halogenation and from amines by forming diazonium salt.
- Aryl halides are not as reactive as alkyl halides for nucleophilic substitution reactions. They may react with moderate base such as NaOH at high temperature and high pressure or with very strong base such as NaNH₂.
- Aryl halides are activated by presence of *ortho* and/or *para* strong electron withdrawing groups.

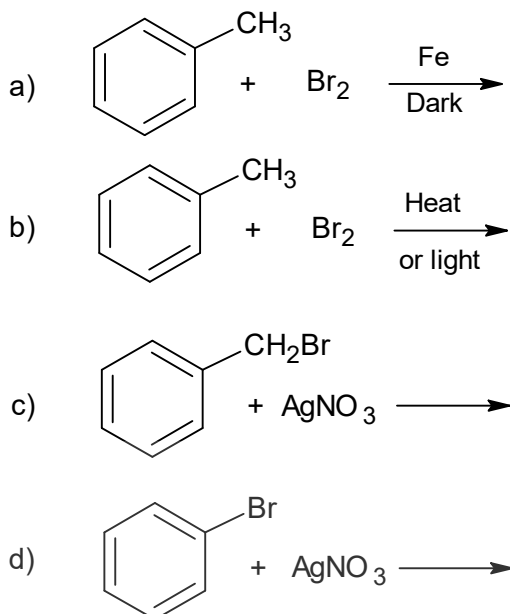
Nucleophilic aromatic substitutions in aryl halides do not follow S_N1 and S_N2 pathways. These reactions occur by two different mechanisms: The addition-elimination mechanism and the benzyne intermediate mechanism.

The aromatic ring to which halogen is attached can undergo typical electrophilic aromatic substitution reactions. Halogen group is deactivating and *ortho*, *para* directing.

- Aryl halides react with magnesium to form aryl magnesium halides called the Grignard reagents.

14.7 TERMINAL QUESTIONS

1. Complete the equation for each of the following reactions. Write only major monohalogen substituted product in each case.



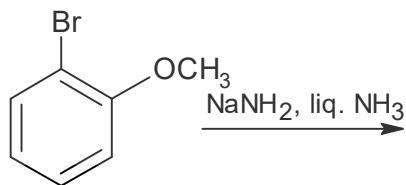
2. Which of the following compounds undergo S_N2/S_N1 reaction? Explain.

- a) Benzyl chloride;
- b) Chlorobenzene;
- c) Chloroethene;
- d) Chloroethyne.

3. Write the equation for each of the following reactions:

- a) 2,4-dinitrochlorobenzene and sodium hydroxide
- b) 2,4-dinitrochlorobenzene and sodium phenoxide
- c) 2,4-dinitrochlorobenzene and ammonia
- d) Chlorobenzene and sodium amide (sodamide).

4. In the following reaction only *meta* isomer is formed though this reaction undergoes benzyne mechanism. Explain.



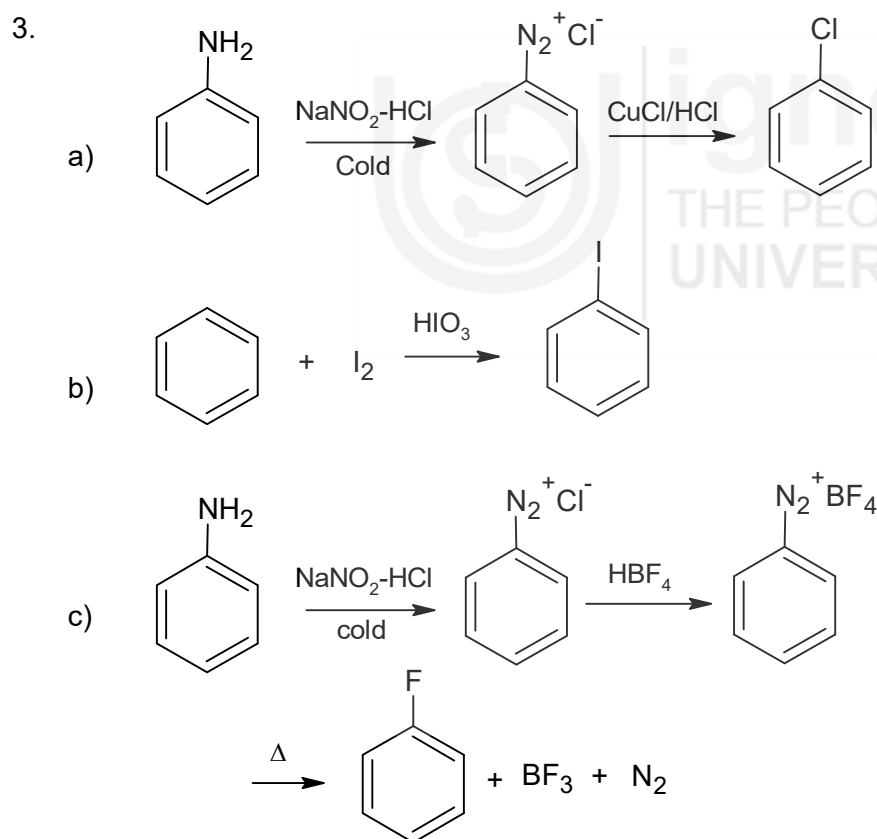
- 5. Although chlorine is an electron withdrawing group, yet it is *ortho*-, *para*-directing in electrophilic aromatic substitution reactions. Why?
- 6. What happens when?
 - (i) Iodobenzene is heating with copper powder,
 - (ii) bromobenzene is heated with Mg,
 - (iii) chlorobenzene is subjected to hydrolysis,

- (iv) Chlorobenzene is treated with alkyl halide in the presence of sodium metal,

14.8 ANSWERS

Self Assessment Questions

- The carbon-halogen bond in aryl halides is shorter and stronger than C—X bond of alkyl halide because of the (i) carbon atom of C—X bond is sp^2 hybridized (having higher s character), (ii) resonance effect causes partial double bond character in C—X bond. Therefore, it is difficult to break during substitution reaction. Few more factors for low reactivity of aryl halide are: poor bond polarity of C—X bond, unfavorable geometry for back side attack of nucleophile due to benzene ring and difficulty in generation of phenyl cation.
- There are two main reason beside C—X bond strength: (i) formation of phenyl cation in case of aryl halides is difficult (S_N1 condition is not fulfilled), (ii) Back side attack on C—X carbon by nucleophile is not possible because of the electron rich aromatic ring (S_N2 condition is not fulfilled).

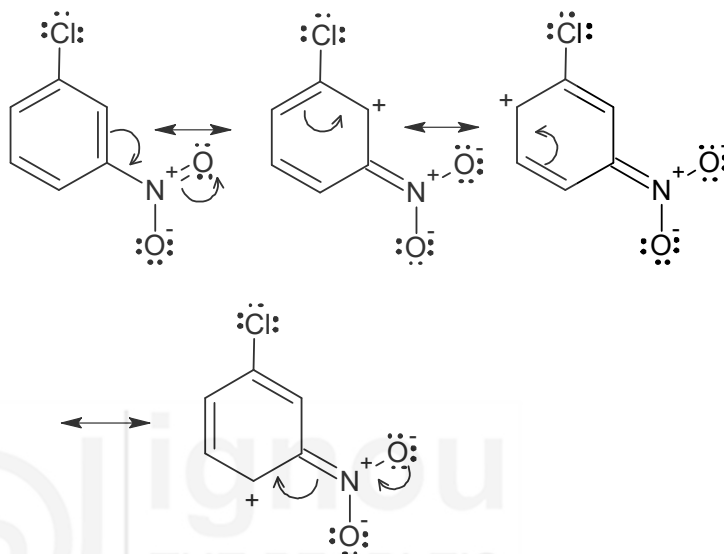


- There are two main factors which are responsible for the lower dipole moment for the C—Cl bond in chlorobenzene than the dipole moment of the same bond in cyclohexyl chloride:
 - In chlorobenzene, the carbon attached to chlorine is sp^2 hybridized, on the other hand, in cyclohexyl chloride it is sp^3 hybridized. Because of the higher s character of sp^2 carbon, it is more

electronegative than sp^3 carbon and hence it has fewer tendencies to release electron to chloride atom. This in turn will make the dipole moment weaker when we compare with sp^3 hybridized C-Cl bond.

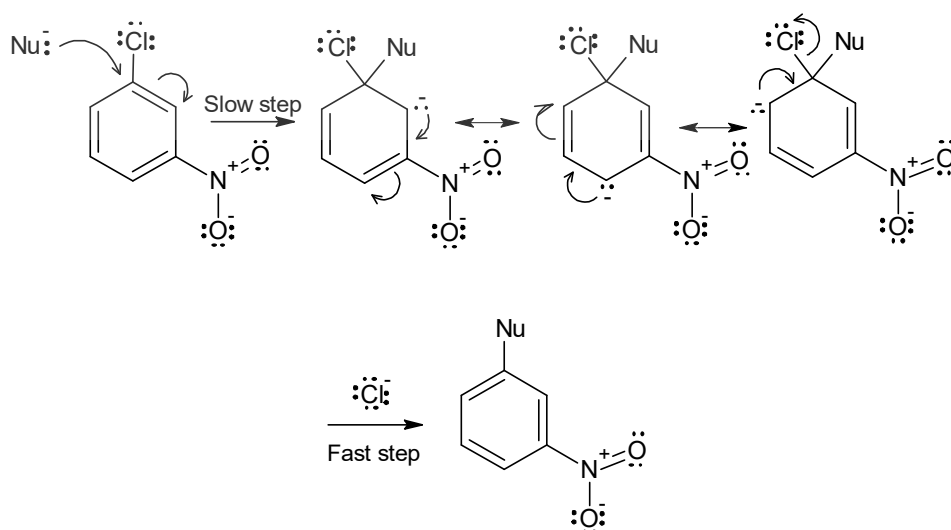
- ii) Delocalisation of lone pairs of electrons of chlorine atom over the benzene ring causes partial double bond character in C-X bond. Thus, the C-X because of resonance effect is shorter than single bond. The bond length has a direct impact on dipole moment because dipole moment depends on charge and distance.

5. Resonance structures of 1-chloro-3-nitrobenzene:

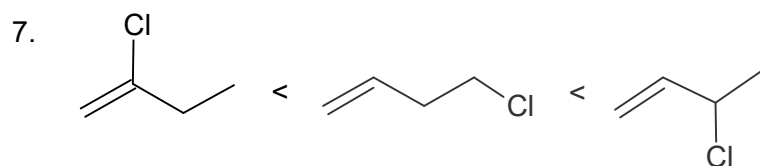
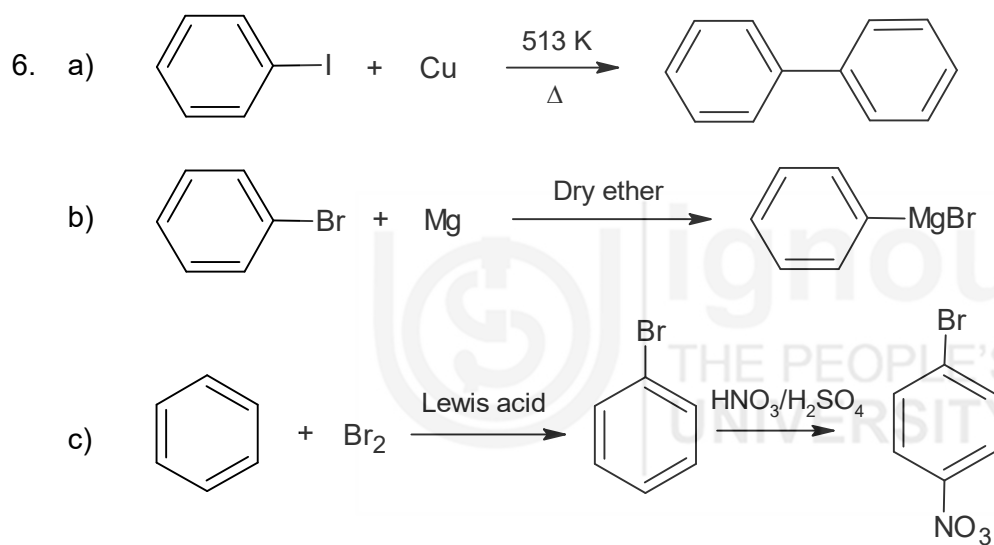
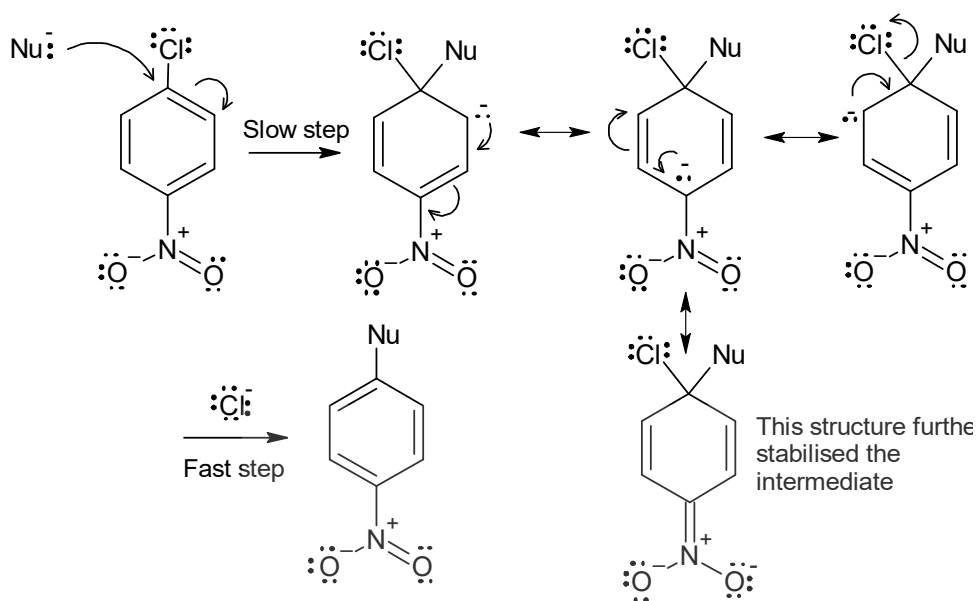
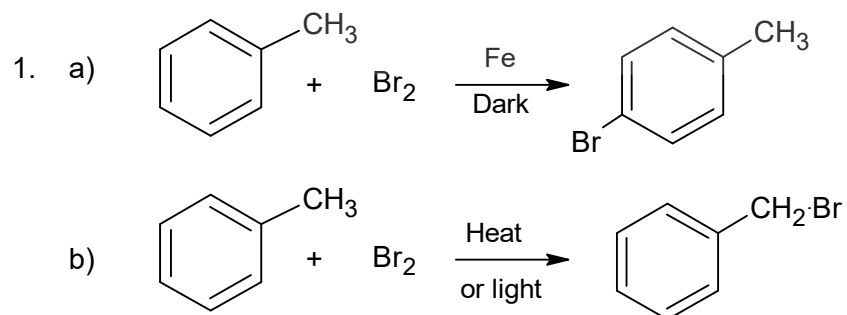


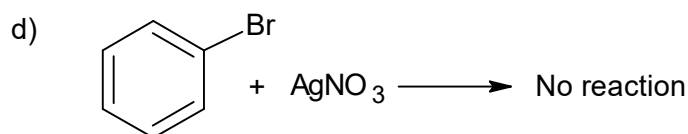
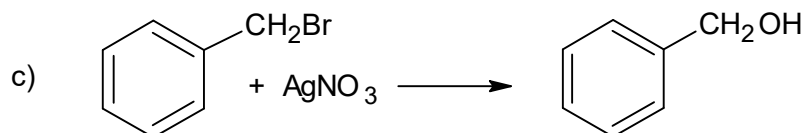
None of the resonating structure bear the +ve charge on carbon atom attached to the -Cl group. But you can see presence of nitro group at 4 position withdraw the electron density from carbon attached to Chlorine atom (See resonance structure III, Sec. 14.4). Further the transition state formed by the attack of a nucleophile is stabilised by the nitro group while in case of 3-chloronitrobenzene, none of the resonating structure bear the negative charge on carbon bearing the $-NO_2$ group.

Nucleophilic attack on 1-chloro-3-nitrobenzene

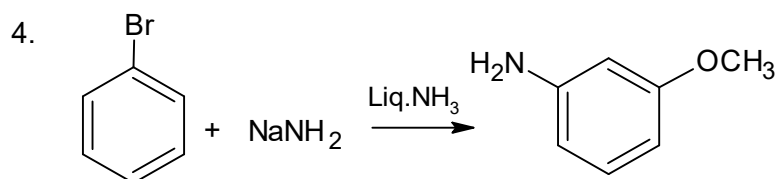
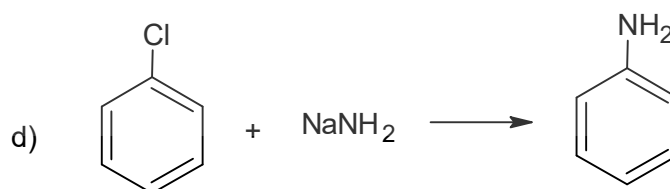
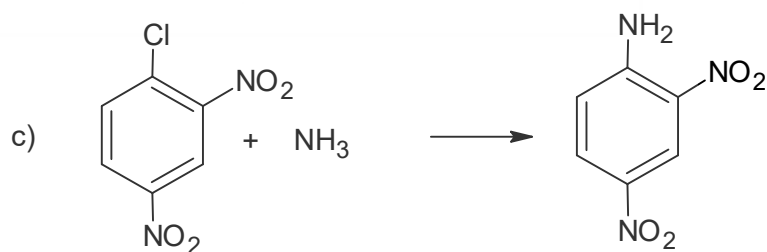
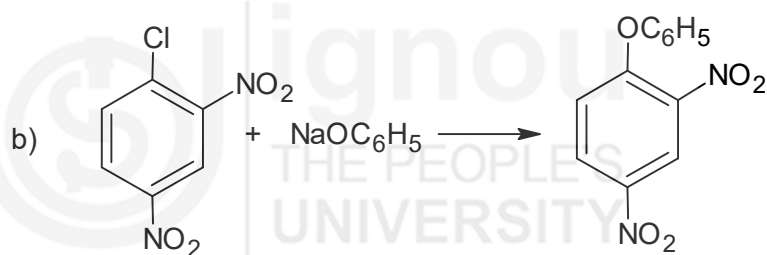
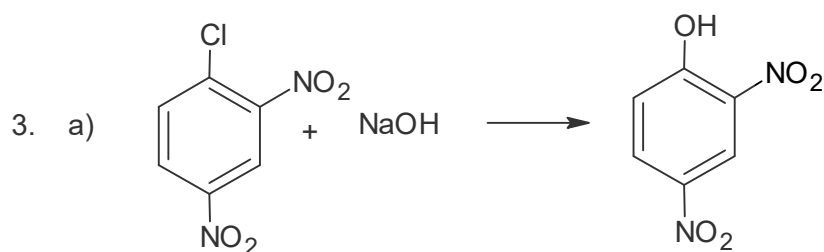


Nucleophilic attack on 1-chloro-4-nitrobenzene

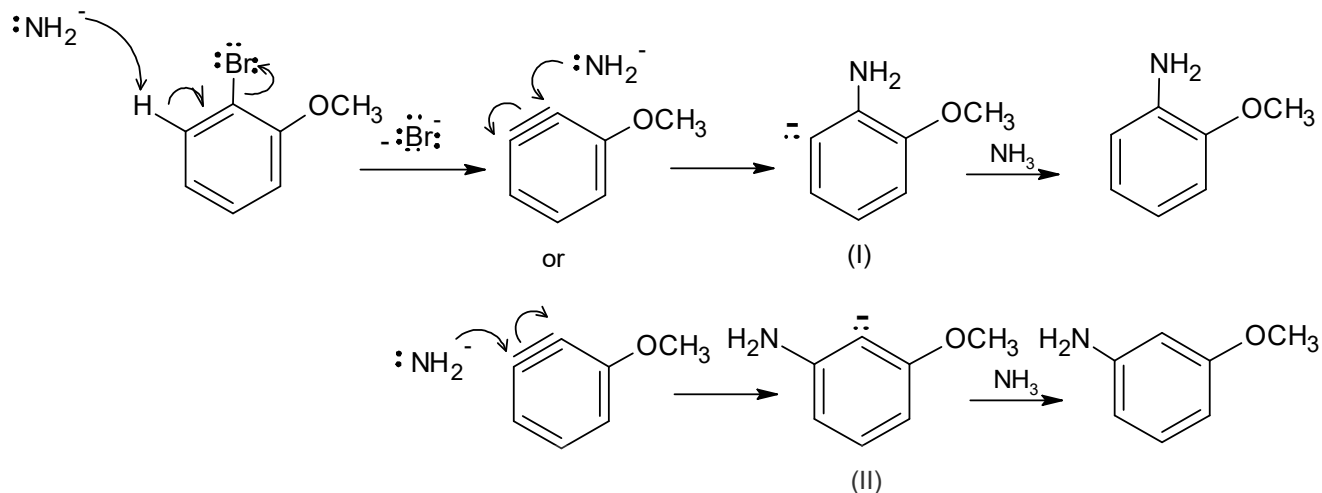
Terminal Questions



2. Formation of carbocations and back side attacks of nucleophile in the case of chlorobenzene, chloroethene and chloroethyne are not feasible, therefore they will not go for S_N1 and S_N2 reactions. On the other hand in benzyl chloride, benzene ring contributes in stabilisation of both carocation and transition state of S_N2 reaction formed during S_N1 and S_N2 reactions. So benzyl chloride will go for S_N1/S_N2 reaction.

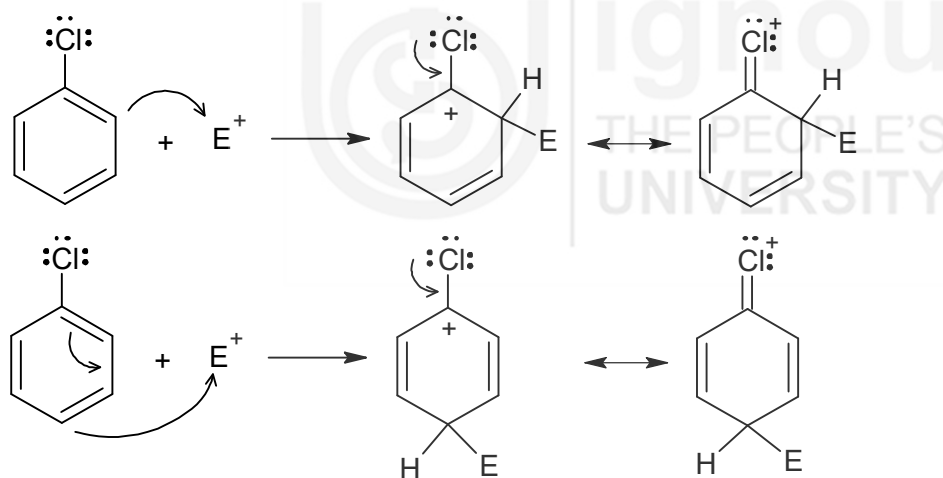


Consider the mechanism of the reactions.

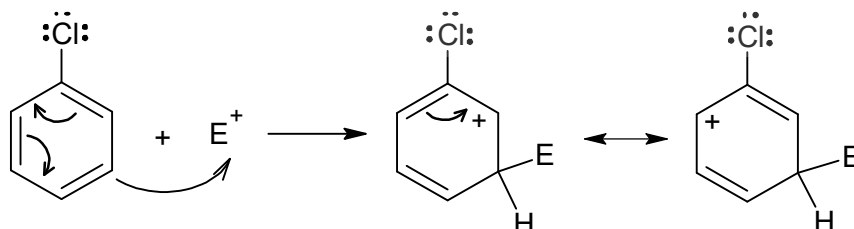


The carbanion (II) formed after amide addition to the intermediate benzyne is stabilised by the electron-withdrawing effect of the methoxy, therefore it is formed regio-selectively. Thus, in this reaction, only one product, i.e. 3-methoxyaniline (*m*-anisidine) is formed.

5. In chlorobenzene, Inductive effect deactivates the benzene ring, but it is *ortho* and *para* directing for electrophilic substitution reactions because of the resonance effect. Carbocation formed after electrophilic attack is more stabilised when it is attacked by an electrophile on *ortho* or *para* position.



Above shown contribution of chlorine atom in resonance stabilisation is not feasible for *meta* attack.



6. i) biphenyl is formed
ii) phenylmagnesium bromide is formed

- iii) at normal temperature there is no reaction but on heating at 573 K and at pressure 238 atm with aqueous NaOH it forms phenol.
- iv) alkylbenzene is formed.

